

Analytical Data Report: Perfluorinated Compounds in Water Samples Collected from Public Water Supplies Near Decatur, Alabama

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Analysis Date: November 17-20, 2008

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Reporting Conventions: Samples less than the method detection limit (MDL) reported as '<MDL.' Samples greater than MDL, but less than limit of quantitation (LOQ), reported in italics followed by '(J)'. Samples exceeding the LOQ are reported without qualification. See accompanying page for collection, preparation, analysis and quality-assurance (QA) practices and definitions. Analyte acronyms reported below are perfluorooctanoic acid (C8), ¹³C₈-perfluorooctanoic acid (an internal recovery standard; M8C8), perfluorodecanoic acid (C10), perfluorobutane sulfonate (PFBS), and perfluorooctane sulfonate (PFOS).

Disclaimer: These data were generated using a developmental method that has not been validated. Available QA information suggests that PFOA, PFOS and PFBS data accurately represent the quality of the sampled waters, but there is some uncertainty for PFDA. See discussion for details.

Water System Source or Handling for Controls	Name	Statistic	---Analyte Concentrations (pg/g)---					M8C8 Recov.
			C8	M8C8	C10	PFBS	PFOS	
Moulton	PWS01	Mean	4.49(J)	ND	<1.93	8.37(J)	7.88(J)	
Turkey Creek		Standard Deviation	1.95	0.00	0.49	2.62	4.82	
Raw		COV	0.43		2.42	0.31	0.61	
		Count	6	6	6	6	6	
Moulton	PWS02	Mean	<4.26	ND	<1.93	4.74(J)	<6.49	
Sinking Creek		Standard Deviation	1.85	0.00	0.62	2.51	1.88	
Raw		COV	0.81		2.42	0.53	0.89	
		Count	6	6	6	6	6	
Moulton	PWS02Dup.	Mean	<4.26	ND	<1.93	5.06(J)	<6.49	
Sinking Creek		Standard Deviation	1.46	0.00	1.04	1.47	2.65	
Raw		COV	0.42		2.42	0.29	1.11	
		Count	6	6	6	6	6	
Moulton	PWS03	Mean	<4.26	ND	<1.93	5.04(J)	<6.49	
Sinking Creek		Standard Deviation	1.56	0.00	0.85	0.75	1.02	
Finished		COV	0.52		2.42	0.15	2.42	
		Count	6	6	6	6	6	
West Morgan/East Lawrence	PWS04	Mean	27.61	ND	<1.93	76.81	25.35	
Raw		Standard Deviation	5.99	0.00	1.22	5.58	5.21	
		COV	0.22		2.42	0.07	0.21	
		Count	6	6	6	6	5	
West Morgan/East Lawrence	PWS05	Mean	25.70	ND	<1.93	72.44	18.40(J)	
Finished		Standard Deviation	3.61	0.00	1.68	8.09	1.93	
Plant Kitchen		COV	0.14		2.42	0.11	0.11	
		Count	6	6	6	6	4	
West Morgan/East Lawrence	PWS06	Mean	24.98	ND	<1.93	70.53	20.94	
Finished		Standard Deviation	4.80	0.00	1.49	5.91	8.33	
Operation Room		COV	0.19		0.80	0.08	0.40	
		Count	6	6	6	6	4	
Decatur	PWS07	Mean	<4.26	ND	<1.93	<2.87	<6.49	
Raw		Standard Deviation	1.49	0.00	0.63	1.43	2.48	
		COV	0.44		2.42	2.42	1.57	
		Count	6	6	6	6	6	
Decatur	PWS08	Mean	<4.26	ND	<1.93	<2.87	ND	
Finished		Standard Deviation	1.84	0.00	1.20	1.57	0.00	
		COV	0.42		2.42	2.42		
		Count	6	6	6	6	6	
Not opened in field	Trip Blank	Mean	<4.26	ND	<1.93	ND	ND	
		Standard Deviation	0.36	0.00	0.68	0.00	0.00	
		COV	1.56		1.60			
		Count	6	6	6	6	6	
Opened & transferred in field	Field Exch.Blk	Mean	<4.26	ND	<1.93	<2.87	<6.49	
		Standard Deviation	0.80	0.00	0.45	0.90	0.53	
		COV	1.25		1.55	2.42	2.42	
		Count	6	6	6	6	6	
Polished lab water	Lab Blank	Mean	<4.26	ND	<1.93	ND	ND	
		Standard Deviation	0.34	0.00	0.15	0.00	0.00	
		COV	1.17		1.88			
		Count	6	6	6	6	6	
Public water at lab	Lab Tap	Mean	<4.26	ND	<1.93	<2.87	<6.49	
		Standard Deviation	1.53	0.00	1.38	1.60	1.30	
		COV	0.54		1.62	2.42	0.98	
		Count	6	6	6	6	5	
Field Equipment Center	Region 4	Mean	<4.26	ND	<1.93	<2.87	ND	
		Standard Deviation	0.80	0.00	0.82	1.50	0.00	
		COV	0.21		1.58	2.42		
		Count	6	6	6	6	6	%
Went to field, left unopened spiked with mass-labeled C8 at 102 ppt	Field Spike	Mean	<4.26	108.23	<1.93	ND	ND	106
		Standard Deviation	0.34	9.70	0.24	0.00	0.00	
		COV	1.76	0.09	2.42			
		Count	6	6	6	6	6	

**Collection, Preparation, Analysis and Quality-Assurance Practices for
Analysis of Perfluorinated Compounds in Water Samples Collected
from Public Water Supplies Near Decatur, Alabama**

Collection: All sampling equipment was rinsed 3x in methanol before the sampling trip. Water samples were collected in HDPE sample bottles after rinsing 3x in the water to be sampled. When water was collected from a flowing source, the sample was collected directly from flow. When water was collected from a pool, as opposed to flowing from a tap, for example, disposable nitrile gloves that had been rinsed 3x in methanol were donned. The samples were kept in a cooler without any cooling effort. No preservatives were used.

Quality Assurances in Field: A field spike consisting of 102 pg/g (ppt) of $^{13}\text{C}_8$ -perfluorooctanoic acid (M8C8) was transported to the field and back to document recovery of a known concentration. A field blank consisting of deionized water polished by elution through a solid-phase extraction (SPE) cartridge was transported to the field and back; this blank was not opened in the field. An identical field blank was transported to the field, transferred to another sample bottle and returned to the laboratory. At one sample location, Moulten, Sinking Creek, raw water, a duplicate sample was collected. A water sample was collected from the EPA Field Equipment Center in Athens, GA for comparison to the sampled systems.

Sample Preparation and Analysis: This is a developmental method that has not been validated. All sample preparation was performed on a mass basis for maximum accuracy. A 9.88 ml aliquot of sample was transferred to an HDPE vial. This aliquot was spiked with ~0.138 g of 96%/4% acetonitrile/water containing mass-labeled matrix internal standards at 6.1 ng/g. This treatment yielded samples consisting of about 99% water and 1% acetonitrile, by mass, containing 84 pg/g of matrix internal standards, the same concentration that the calibration standards contain. Mass-labeled matrix internal standards included (M+4)perfluorobutanoic acid, (M+2)perfluorohexanoic acid, (M+4)PFOA, (M+5)perfluorononanoic acid, (M+2)perfluorodecanoic acid (PFDA or C10), (M+2)perfluoroundecanoic acid, (M+2)perfluorododecanoic acid, (M+2)6:2-fluorotelomer unsaturated carboxylic acid (FTUCA), (M+2)8:2-FTUCA, and (M+2)10:2-FTUCA. Spiked samples were transferred to polypropylene autosampler vials. All samples were analyzed by ultra-performance liquid chromatography, tandem mass spectrometry operated in negative electrospray-ionization mode. Analytes included perfluorocarboxylic acids C4 through C14, FTUCAs 6:2, 8:2 and 10:2, and perfluorosulfonates C4 (PFBS), C6, C7 and C8 (PFOS). Water samples were collected from the laboratory tap for comparison to the sampled systems. Deionized water was polished by elution through an SPE cartridge to represent zero concentration of the analytes.

Quality Assurances in Laboratory: Samples were prepared in replicate with each replicate spiked with matrix internal standards independently of the other to reflect variation from spiking. Each replicate was run 3 times so that each water sample was represented by 6 analytical runs for each analyte. Samples were interspersed with standards and blanks. Standards were run 6 times at each of 8 or 9 levels ranging from 0.9 pg/g to 230 pg/g.

All analytical sample data were scanned at a reconnaissance level. Based on this review as well as data on perfluorinated compounds in sludge and soil samples from an earlier effort, careful review of quantitation was performed on PFOA, $^{13}\text{C}_8$ -PFOA (M8C8), PFDA, PFBS and PFOS using 1/x regression with resulting correlation coefficients of $r > 0.99$ in all cases. Analytical results for these compounds were carefully reviewed for all samples as well. The analytes PFOA, M8C8 and PFDA were quantitated by isotopic dilution using their corresponding matrix internal standards. The analyte PFBS was quantitated using (M+2)C6 as the matrix internal standard and PFOS was quantitated using (M+2)C10.

Method detection limits (MDLs) and limits of quantification (LOQs) were calculated using the collected water samples and the polished deionized laboratory water. The sample data were chosen based on their status as having analytical concentrations that were low, but above the MDL eventually calculated. The blank data were chosen based on their status as representing the highest background for a grouped sequence of six blanks run interspersed among the samples; selection of these blanks is conservative with respect to defining detection limits. These are the values to calculate the MDLs and LOQs:

Instrument Response Peak Ratio (Analyte/Internal Standard)					
Repeated	C8	mC8	C10	PFBS	PFOS
Measures of	Sample	Sample	Sample	Sample	Sample
Samples	PWS01	FldSpk	PWS06	PWS02	PWS01
1	0.065	1.578	0.033	0.026	0.056
2	0.042	1.475	0.029	0.032	0.068
3	0.059	1.46	0.039	0.025	0.104
4	0.038	1.225	0.025	0	0.038
5	0.076	1.345	0	0.025	0.091
6	0.092	1.318	0.026	0.015	0
Blanks					
11	0.025	0	0	0	0
12	0.022	0	0	0	0
13	0.019	0	0	0	0
14	0.009	0	0	0	0
15	0.009	0	0	0	0.004
16	0.009	0	0.007	0	0

MDLs and LOQs were calculated using American Chemical Society conventions (Keith et al., 1983), altered following the approach of Washington (2007) to include uncertainty imparted from background detections in blanks that commonly are encountered with these analytes. This adjustment is conservative for calculating detection limits.

Limit	C8	mC8	C10	PFBS	PFOS
MDL (pg/g)	4.26	13.36	1.93	2.87	6.49
LOQ (pg/g)	9.81	39.68	5.52	8.51	19.11

There is uncertainty regarding the quality of the PFDA data reported herein using this developmental method that has not been validated. This is true because the peak areas of the matrix internal standards in the samples decrease with increasing chain length, both in an absolute sense and relative to the calibration standards. The following table reports the average of three internal-standard peak areas for arbitrarily chosen samples and standards.

Compound Type	Internal Standard	Mean of 3 Peak Areas		
		Sample	Standard	Smpl/Stnd
Perfluorocarboxylic Acids	C4	465	466	1.00
	C6	596	612	0.97
	C8	461	752	0.61
	C9	532	1274	0.42
	C10	336	1590	0.21
	C11	83	1625	0.05
	C12	11	1087	0.01
Fluorotelomer Acids				
	6:2	559	747	0.75
	8:2	325	961	0.34
	10:2	63	759	0.08

The instrument response for the samples falls off precipitously starting at C9 or C10. Such a decrease in response could reflect matrix suppression in which case reported values should be reasonable. Alternatively, the decrease in response could reflect sorption of longer-chained compounds to the sample container, in which case these compounds would be under-reported. As a consequence of this observation, we recommend that the PFDA data we report be viewed with special prudence.

References:

- Keith, LH, Libby, RA, Crummett, W, Taylor, JK, Deegan, Jr., J, Wentler, G. 1983. Principles of environmental analysis. *Analytical Chemistry*. 55. 2210-2218.
- Washington, JW, Ellington, JJ, Jenkins, TM, Evans, JJ. 2007. Analysis of perfluorinated carboxylic acids in soils: Detection and quantitation issues at low concentrations. *Journal of Chromatography A*. 1154. 111-120.